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Supplementary Materials for

Uniform Patchy and Hollow Rectangular Platelet Micelles from Crystallizable Polymer Blends

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Materials and Methods

Polymer Synthesis

All polymerizations were carried out in an inert atmosphere glovebox. PFS_{43} (M_n = 10,500 g/mol, PDI = 1.04), PFS_{20} (M_n = 4,800 g/mol, PDI = 1.03), PFS_{49}-*b*-$PDMS_{504}$ (M_n = 49,200 g/mol, PDI = 1.09), PFS_{28}-*b*-$PDMS_{560}$ (M_n = 48,200 g/mol, PDI = 1.02), $PFDMS_{132}$-*b*-$PDMS_{1364}$ (M_n = 132,900 g/mol, PDI = 1.10), PFS_{55}-*b*-$PMVS_{825}$ (M_n = 84,200 g/mol, PDI = 1.09), PFS_{36}-*b*-$P2VP_{502}$ (M_n = 61,400 g/mol, PDI = 1.20), PFS_{20}-*b*-$P2VP_{444}$ (M_n = 51,500 g/mol, PDI = 1.30), PFS_{34}-*b*-$P2VP_{272}$ (M_n = 36,800 g/mol, PDI = 1.07), PFS_{36}-*b*-$PnBMA_{756}$ (M_n = 116,000 g/mol, PDI = 1.27), PFS_{29}-*b*-($PDMS_{652}$-*r*-R_{19}) (M_n = 68,000 g/mol, PDI = 1.23), PFS_{29}-*b*-($PDMS_{652}$-*r*-G_{19}) (M_n = 63,700 g/mol, PDI = 1.22) and PFS_{29}-*b*-($PDMS_{652}$-*r*-B_{19}) (M_n = 62,100 g/mol, PDI = 1.17) were synthesized as previously reported (*27*, *32-35*) [PFS = poly(ferrocenyldimethylsilane), PDMS = poly(dimethylsiloxane), PMVS = poly(methylvinylsiloxane), P2VP = poly(2-vinylpyridine), PnBMA = poly(n-butylmethacrylate); R, G, and B refer to PMVS functionalized with the fluorescent dyes in ref. 27; the subscripts refer to the degrees of polymerization]. Gel permeation chromatography (GPC) was carried out on a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph using THF as the eluent. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurements were performed using a Bruker Ultraflextreme running in linear mode. To determine the molar mass of the block copolymers, aliquots of the first block (PFS) were taken and the absolute molar mass of the first block was determined by GPC or MALDI-TOF. The absolute molecular weights of the diblocks were then determined by combining the molecular weight M_n of the first block with the block ratio of the diblock copolymer obtained by integration of the ^1H NMR spectroscopic signal intensities of the respective blocks.

Characterization

Bright field transmission electron microscopy (TEM) images were obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. Samples were prepared by dropping 10 μL aliquot of the solution onto carbon-coated copper grids resting on a piece of filter paper to remove excess solvent. No staining of the samples was necessary. Images were analyzed using the ImageJ 1.48i software package developed at the US National Institute of Health. Atomic force microscopy (AFM) analyses were performed in ambient conditions using a Bruker Multimode VIII atomic force microscope equipped with a ScanAsyst-HR fast scanning module and a ScanAsyst-Air-HR probe (tip radius, 2 nm), utilizing peak force feedback control. Samples were prepared by dropping 10 μL aliquot of the solution onto freshly cleaved mica substrates. Energy dispersive X-ray (EDX) spectroscopy was performed using an Aztec X-Max 80 mm^2 Silicon drift detector (Oxford Instruments) attached to a JEOL2100F field emission scanning transmission electron microscope (Chemistry Imaging Facility at University of Bristol (UoB) with equipment funded by UoB and EPSRC (EP/K035746/1 and EP/M028216/1)). Confocal laser scanning microscopy (CLSM) images were obtained using a Leica SP8 AOBS confocal laser scanning microscope, which was attached to a Leica DM I6000 inverted epifluorescence microscope with adaptive focus control to correct focus drift during time-courses and a

63× glycerol immersion objective lenses (numerical aperture, NA = 1.3). For CLSM analysis, fluorophores from red (R), green (G) and blue (B) dye-functionalized polymers were excited using a HeNe laser operating at 594 nm, an argon laser operating at 488 nm and an ultraviolet diode laser operating at 405 nm, respectively. Images were obtained using digital detectors with observation windows of 605–700 nm for R, 500–570 nm for G and 415–470 for B. Structured illumination microscopy (SIM) was performed using a Zeiss Elyra PS. 1 microscope with a 100× oil immersion objective lens (NA = 1.46), with fluorophores from R, G and B polymers excited by diode lasers operating at 642 nm, 488 nm and 405 nm, respectively. Raw images were acquired at three grating angles, and with observation windows of 655–800 nm, 495–575 nm and 420–480 nm for R, G and B. The resulting outputs from both CLSM and SIM were obtained as digital false-colour images, and colour coded as red, green and blue, respectively. For imaging of the multiblock comicelles, the output power of each laser was varied until the fluorescence of all blocks could be observed at approximately equal brightness. To prepare a sample, a rectangular capillary tube (0.1 × 1.0 × 50 mm, borosilicate glass, CM Scientific) was immersed in the sample solution until it was fully filled. The capillary tube was then placed on a glass microscopy slide where a small amount of epoxy adhesive (Araldite) was used to seal it at either end and fix it in place.

Preparation of Cylindrical Micelle Seeds

Long polydisperse cylindrical micelles were firstly prepared by dissolution of the polymer solid in a selective solvent (0.5 mg/mL) by stirring at 60 °C for ca. 30 min following by an aging process at room temperature for 1 day. The micelles were then fragmentized by sonication in an ultrasonic cleaning bath (Bandelin Sonorex Digitec DT 225H, 35 kHz, 160 W output) at 0 °C or using a probe ultrasonic processor (Hielscher UP50H operating at 30 kHz and 50 W equipped with a Hielscher MS1 titanium sonotrode) at -78 °C in a dry ice-acetone bath. Monodisperse cylindrical micelles with variable lengths were subsequently obtained by a self-seeding process at various elevated temperatures (*36*). It was found that the PFS-*b*-P2VP cylindrical micelle seeds prepared in isopropanol (iPrOH) after self-seeding may dissociate in 1:3 hexane/iPrOH at 45 °C during the seeded growth of the platelet micelles as a result of solvent-induced self-seeding (*36*), since hexane is a better solvent than iPrOH for the PFS core-forming block. To prepare robust cylindrical micelle seeds the fragmentized PFS-*b*-P2VP micelle solution in iPrOH was diluted by a mixture of hexane and iPrOH to 0.25 mg/mL with final hexane to iPrOH volume ratio of 1:3 prior to self-seeding.

Seeded Growth / Living Crystallization-Driven Self-Assembly (CDSA) of PFS_{49}-*b*-$PDMS_{504}$/PFS_{43} Blends in Hexane

Self-assembly of blends of PFS block copolymers and homopolymers in the absence of seeds yields a range of different composition-dependent morphologies that includes polydisperse 2D platelets (37).

To 1 mL of a solution of the cylindrical micelle seeds derived from PFS_{28}-*b*-$PDMS_{560}$ (0.01 mg/mL in hexane) was added a specified amount of a mixture of the PFS_{49}-*b*-$PDMS_{504}$ and PFS_{43} unimers (1:1 to 20:1 mass ratios) as a 10 mg/mL (overall concentration) THF solution, followed by vigorous shaking for 5 s using a vortex agitator. The solution was then allowed to age at room temperature for 1 day. See fig. S2.

Seeded Growth / Living CDSA of PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} Blends in Hexane

To 1 mL of a solution of the cylindrical micelle seeds derived from PFS_{28}-*b*-$PDMS_{560}$ or PFS_{132}-*b*-$PDMS_{1364}$ (0.01 mg/mL in hexane) was added a specified amount of a mixture of the PFS_{28}-*b*-$PDMS_{560}$ and PFS_{20} unimers (1:1 mass ratio) as a 10 mg/mL (overall concentration) THF solution, followed by vigorous shaking for 5 s using a vortex agitator. The solution was then allowed to age at room temperature for 1 day. See fig. S3 and fig. S4.

Seeded Growth/ Living CDSA of PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} Blends with Various PFS_{36}-*b*-$P2VP_{502}$ to PFS_{20} Mass Ratios

The solution of the cylindrical micelle seeds derived from PFS_{28}-*b*-$PDMS_{560}$ was firstly diluted by hexane and iPrOH to 0.0025 mg/mL. The final hexane to iPrOH volume ratio was set to 1:3. To a 7 mL screw-cap vial was added 2 mL of the seed solution and the solution was heated to 45 °C using a block heater (Grant QBH2). After 10 min, a specified amount of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blend unimers with 8:1, 4:1, 2:1 and 1:1 mass ratio, respectively, was added as a 10 mg/mL (overall concentration) THF solution, followed by vigorous shaking for 5 s using a vortex agitator. The solution was allowed to age at 45 °C for 1 h and then cooled slowly to room temperature in the heating block and allowed to age at room temperature for 1 day. See fig. S5, D-E.

As control experiments (all initially performed at 45 °C) (i) to 2 mL of 1:3 (v/v) hexane/iPrOH without any micelle seeds was added a specified amount of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blend unimers (1:1 mass ratio) as a 10 mg/mL (overall concentration) THF solution, followed by vigorous shaking and aging; (ii) to 2 mL of the seed solution in 1:3 (v/v) hexane/iPrOH was added a specified amount of the PFS_{20} homopolymer only as a 10 mg/mL THF solution, followed by vigorous shaking and aging; (iii) to 2 mL of the seed solution in 1:3 (v/v) hexane/iPrOH was added a specified amount of the PFS_{36}-*b*-$P2VP_{502}$ diblock copolymer only as a 10 mg/mL THF solution, followed by vigorous shaking and aging. See fig. S5, A-C.

Seeded Growth / Living CDSA of PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} and PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} Blends in Various Mixtures of Hexane and iPrOH

The solution of the cylindrical micelle seeds derived from PFS_{28}-*b*-$PDMS_{560}$ was firstly diluted by hexane and iPrOH to 0.0025 mg/mL. The final hexane to iPrOH volume ratio was set to 3:1, 2:1, 1:1, 1:2, 1:3 and 1:6, respectively. To a 7 mL screw-cap vial was added 2 mL of the seed solution and the solution was heated to 45 °C using a block heater. After 10 min, a specified amount of the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} or PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blend unimers (1:1 mass ratio) was added as a 10 mg/mL (overall concentration) THF solution, followed by vigorous shaking for 5 s using a vortex agitator. The solution was allowed to age at 45 °C for 1 h and then cooled slowly to room temperature in the heating block and allowed to age at room temperature for 1 day. See fig. S6.

Seeded Growth / Living CDSA as A Route to Low Dispersity Rectangular 2D Platelets (Optimized seeded growth procedure for various blends using different seeds)

Hexane : iPrOH = 1:3 (v/v), diblock copolymer : PFS_{20} = 1:1 (mass ratio), initial temperature = 45 °C were found to be the optimized condition for the formation of rectangular platelets from various blends (including PFS_{36}-*b*-$PnBMA_{756}$/PFS_{20}, the fluorescent polymer blends, and many more others) using cylindrical micelle seeds derived from a series of block copolymers, such as PFS_{28}-*b*-$PDMS_{560}$, PFS_{132}-*b*-$PDMS_{1364}$, PFS_{20}-*b*-$P2VP_{444}$, or PFS_{34}-*b*-$P2VP_{272}$. In a typical process, to 2 mL of the seed solution warmed at 45 °C was added a tunable amount of the blend unimers as a 10 mg/mL (overall concentration) THF solution, followed by vigorous shaking for 5 s using a vortex agitator. The solution was allowed to age at 45 °C for 1 h and then cooled slowly to room temperature in the heating block and allowed to age at room temperature for 1 day. See Fig. 1 and fig. S8.

Near monodispersity is to be expected for a seeded growth process where the "initiation" from the seed is fast and there is no "termination" interfering with the elongation/growth/propagation step (which might be caused by precipitation, for example). The resulting structures under these circumstances should naturally possess a narrow size distribution. This has been established for a range of different BCP systems for the growth of 1D structures and is expected for a "nucleation-elongation process" of which living 1D covalent polymerizations represent the prototypical case (see Ref. 6 for further discussions). In the present work on 2D rectangular structures the narrow size distribution is characterized by a low dispersity in area. Moreover, a plot of area vs unimer:seed ratio is linear as befits a process analogous to a living (1D) covalent polymerization.

Monitoring Seeded Growth / Living CDSA of PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} Blends by TEM

To study the growth mechanism, a series of aliquots of the solution was sampled during the seeded growth. Typically, after the blend unimers were added (at 45 °C), the mixture was vigorously shaken for 5 s using a vortex agitator and a drop aliquot was immediately placed onto a carbon-coated copper grid resting on a piece of filter paper (warmed at 45 °C as well). The vial was moved back to the block heater and aliquots of the solution were taken every 5 – 10 seconds and immediately placed on a series of carbon-coated copper grids. See fig. S7.

Seeded Growth / Living CDSA of PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} Blends in Mixtures of Hexane and Methanol to Create Giant Platelet Micelles

Typically, to 2 mL of 1:3 (v/v) hexane/methanol was added 5 μL of the PFS_{20}-*b*-$P2VP_{444}$ cylindrical micelle seed solution (0.01 mg/mL in iPrOH). Thus the final solvent composition was approximately 1:3 (v/v) hexane/methanol. The solution was heated to 45 °C using a block heater. After 10 min, 5 μL of a THF solution (10 mg/mL, overall concentration) of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blend unimers (1:1 mass ratio) was added, followed by vigorous shaking for 5 s using a vortex agitator. The solution was allowed to age at 45 °C for 2 days prior to cooling to room temperature. See fig. S9.

Sequential Seeded Growth / Living CDSA of PFS_{28}-*b*-$PDMS_{560}$/PFS_{20}, PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} and PFS_{36}-*b*-$PnBMA_{756}$/PFS_{20} Blends

Typically, to a 7 mL screw-cap vial was added 2 mL of a solution of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds in 1:3 (v/v) hexane/iPrOH (0.0025 mg/mL) and the solution was heated to 45 °C using a block heater. After 10 min, specified amounts of the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20}, PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} and PFS_{36}-*b*-$PnBMA_{756}$/PFS_{20} blend unimers (1:1 mass ratio) were sequentially added as 10 mg/mL (overall concentration) THF solutions with interval between two additions of 10 min and vigorous shaking for 5 s using a vortex agitator for each addition. The solution was allowed to age at 45 °C for 1 h and then cooled slowly to room temperature in the heating block and allowed to age at room temperature for 1 day. See Fig. 2 and figs. S12 and S13.

For the preparation of fluorescent rectangular platelets, PFS_{28}-b-$PDMS_{560}$ was simply replaced with PFS_{29}-*b*-($PDMS_{652}$-*r*-R_{19}), PFS_{29}-*b*-($PDMS_{652}$-*r*-G_{19}), or PFS_{29}-*b*-($PDMS_{652}$-*r*-B_{19}). In a typical process, to a 7 mL screw-cap vial was added 2 mL of a solution of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds in 1:3 (v/v) hexane/iPrOH (0.0025 mg/mL) and the solution was heated to 45 °C using a block heater. After 10 min, specified amounts of the fluorescent PFS_{29}-*b*-($PDMS_{652}$-*r*-R_{19})/PFS_{20}, PFS_{29}-*b*-($PDMS_{652}$-*r*-G_{19})/PFS_{20}, PFS_{29}-*b*-($PDMS_{652}$-*r*-B_{19})/PFS_{20} blend unimers (1:1 mass ratio, overall 10 mg/mL in THF), together with the non-fluorescent blend unimers, such as the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blend unimers (1:1 mass ratio) were sequentially added with interval between two additions of 10 min and vigorous shaking for 5 s using a vortex agitator for each addition. The solution was allowed to age at 45 °C for 1 h and then cooled slowly to room temperature in the heating block and allowed to age at room temperature for 1 day. See Fig. 3A.

Crosslinking of P2VP Coronas and Removal of Uncrosslinked Regions

To a 1.5 mL screw-cap vial was added 0.2 mL aliquot of a solution of the rectangular platelet micelles or block comicelles. The vial was flushed with nitrogen and capped and transferred to glovebox. In the glovebox, 1 μL of 1,1,3,3-tetramethyldisiloxane (Sigma-Aldrich) and 1 μL of Karstedt's catalyst (Platinum-divinyltetramethyldisiloxane complex in xylenes with a Pt mass% of 2.1-2.4, ABCR) were added and the solution was shaken for a few seconds and then allowed to age for 1 day (*22*). Typical 2VP : Pt mole ratios in these experiments were ca. 1:2, indicating that a high density of Pt NPs: thus, a high crosslinking density is anticipated throughout the P2VP corona. To remove the uncrosslinked regions, 50 μL of the solution was dried with nitrogen stream and then redispersed in 100 uL of THF. The samples were left in THF for at least 1 day prior to analysis and still retained their structural integrity after 1 year in this solvent. The retention of the structural integrity despite the homopolymer rich composition is attributed to very effective crosslinking by the Pt NPs. The latter appear to be distributed over the whole platelet surface based on the height increase of ca. 5 – 30 nm detected by AFM (compare height profiles in Figure 1C and 1B). After etching with THF, no convincing evidence for the existence of holes in the crosslinked platelet (other than at the previous location of the seed) was detected by high resolution TEM or even after 1 year by high resolution AFM (fig. S10). See Figs. 1 and 2, figs. S10 – S12.

Selective Deposition of Silica Nanoparticles on P2VP Coronas

Silica nanoparticles with average diameter of 70 nm were prepared by a modified Stöber method (*38*). Briefly, 0.2 mL of tetraethyl orthosilicate (Sigma-Aldrich) was

quickly added to a mixture of ethanol (20 mL) and aqueous ammonia (35%, 1 mL). The mixture was vigorously stirred for 10 min and allowed to age at room temperature for 1 day. The solution was then subjected to dialysis against ethanol and further diluted by ethanol to a final volume of 20 mL. In a typical deposition experiment, to 0.1 mL aliquot of a solution of the rectangular platelet micelles or block comicelles was added 5 mL of the silica nanoparticle solution. The mixture was vigorously shaken for 10 s using a vortex agitator and allowed to age at room temperature for 30 min before an aliquot was taken and drop-casted onto a carbon film-coated copper grid. It should be noted that these are qualitative experiments to demonstrate the attachment of the silica particles to the P2VP regions and thus the relative ratio between two components was not specifically controlled. See Fig. 3B.

Manipulation of Rectangular Platelet Micelles and Block Comicelles by Optical Tweezers

To prepare a sample, a rectangular borosilicate capillary tube was filled with the rectangular platelet solution. The capillary tube was then placed on a glass microscopy slide where a small amount of epoxy adhesive (Araldite) was used to seal it at either end and fix it in place. Manipulation experiments were performed on a single beam optical tweezer system. This consisted of a 4 W 1064 nm wavelength titanium sapphire infrared laser beam (coherent 899) expanded to fill an electrically addressed spatial light modulator (Boulder Nonlinear Systems, P512-0785). Each hologram was performed on the graphics card (nVidia Quadro FX 5600) in under 1 ms, with a LABVIEW interface used as a control. The beam subsequently moved through a polarizing beam splitter and imaged onto the back aperture of an objective lens (Zeiss Plan-Neofluor, 100×, NA = 1.3) which focuses it. This created the optical traps, and collected the focused illumination light (50 W halogen bulb) from the sample, with around 40% of the laser beam's power passed by the objective. A beam splitter was used to direct light from the sample to a high-speed CMOS camera (Prosilica, EC1280) while translation of the field of view was achieved with a motorized x-y-z stage. For manipulation, a single rectangular platelet micelle/block comicelle in 1:3 (v/v) hexane/iPrOH was trapped by two beams at either end to control both the direction and position. The platelet was then placed on the surface of the capillary tube, where it was subsequently immobilized due to the hydrogen bonding interactions between the P2VP coronas and the borosilicate substrate (*39*). See fig. S14.

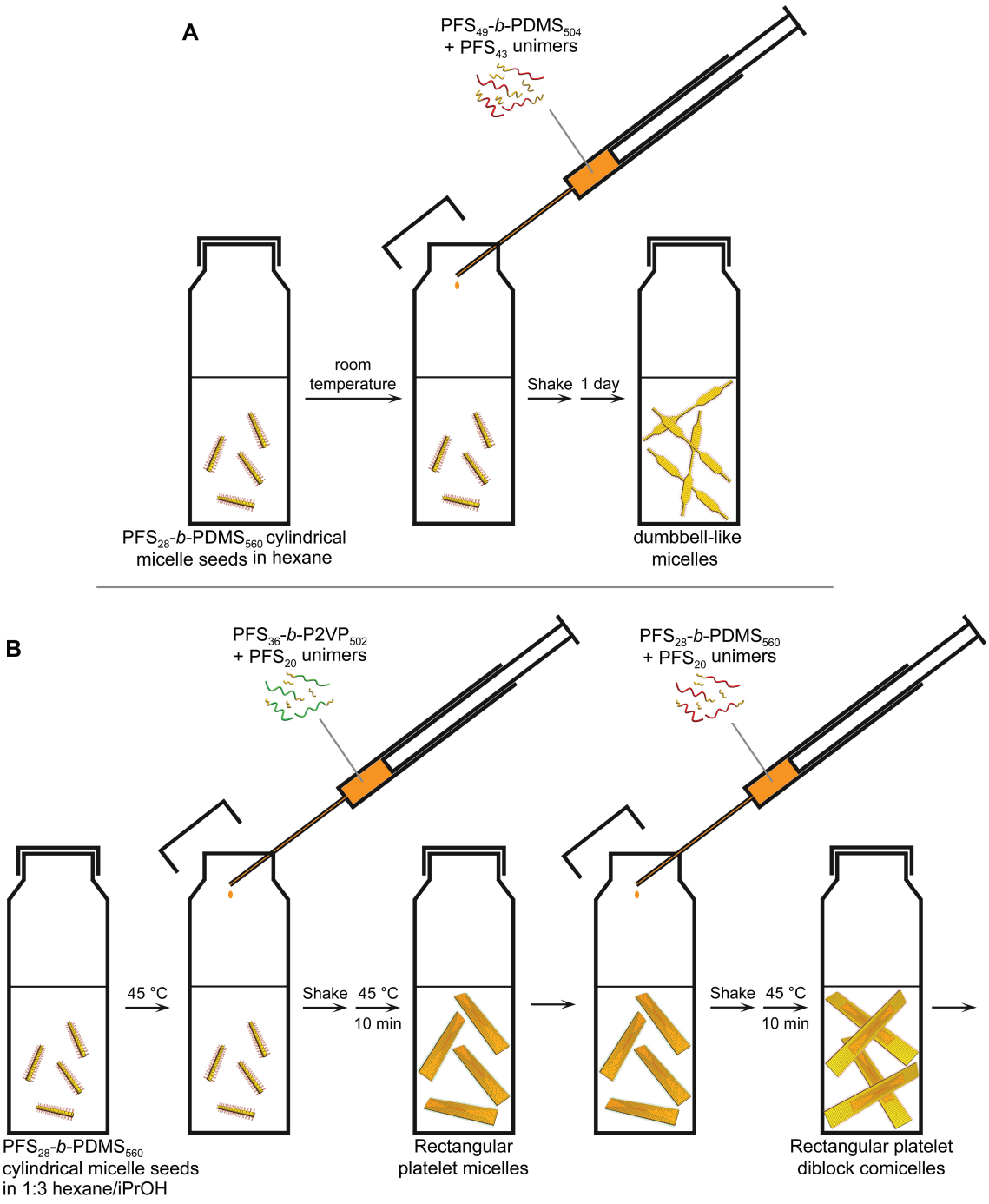

Fig. S1. Experimental approach to prepare (A) dumbbell-like and (B) concentric rectangular platelet block comicelles. In each case the blend unimers were added as a concentrated solution in THF. For complete experimental details see pages S3–S6.

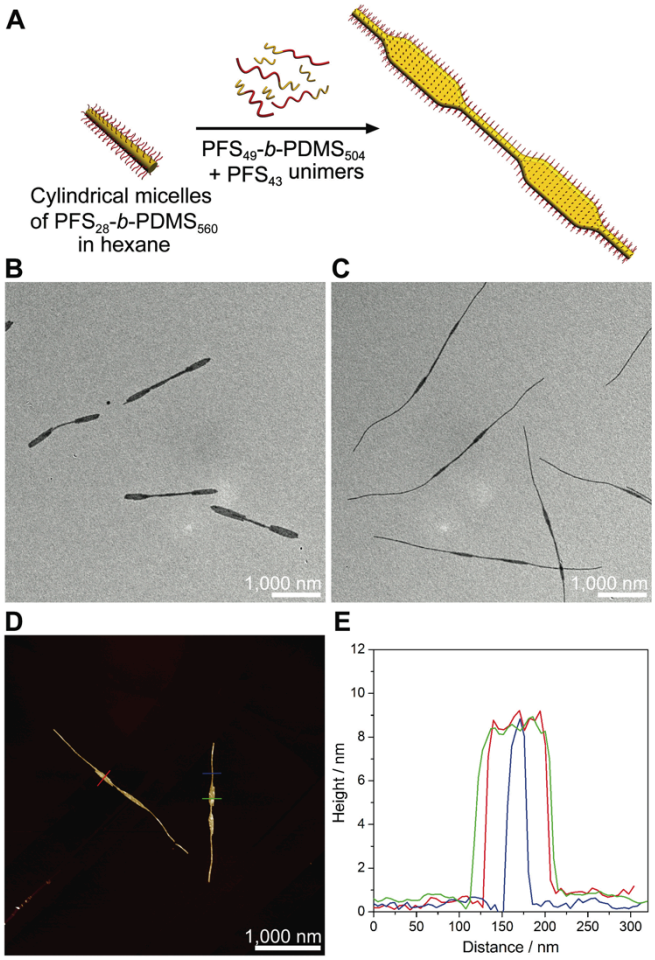

Fig. S2. Dumbbell-like micelles by seeded growth / living CDSA of PFS_{49}-*b*-$PDMS_{504}$/PFS_{43} blends in hexane. The PFS_{49}-*b*-$PDMS_{504}$/PFS_{43} blends only grow from the end of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds, leading to the formation of dumbbell-like micelles with either platelet-like or platelet-cylinder-like end segments. (**A**) Schematic diagram illustrating this process. (**B**) Representative TEM images of dumbbell-like micelles with two platelet-like end segments formed by the PFS_{49}-*b*-$PDMS_{504}$/PFS_{43} (1:1 mass ratio) blend unimers at room temperature. (**C-E**) Representative TEM, AFM height image, and height profiles of dumbbell-like micelles with two platelet-cylinder-like end segments formed by the PFS_{43}-*b*-$PDMS_{504}$/PFS_{43} (10:1 mass ratio) blend unimers at room temperature. The cylindrical seeds used were as follows: (B and C) PFS_{28}-*b*-$PDMS_{560}$ L_n = 680 nm and (D) PFS_{28}-*b*-$PDMS_{560}$ L_n = 230 nm.

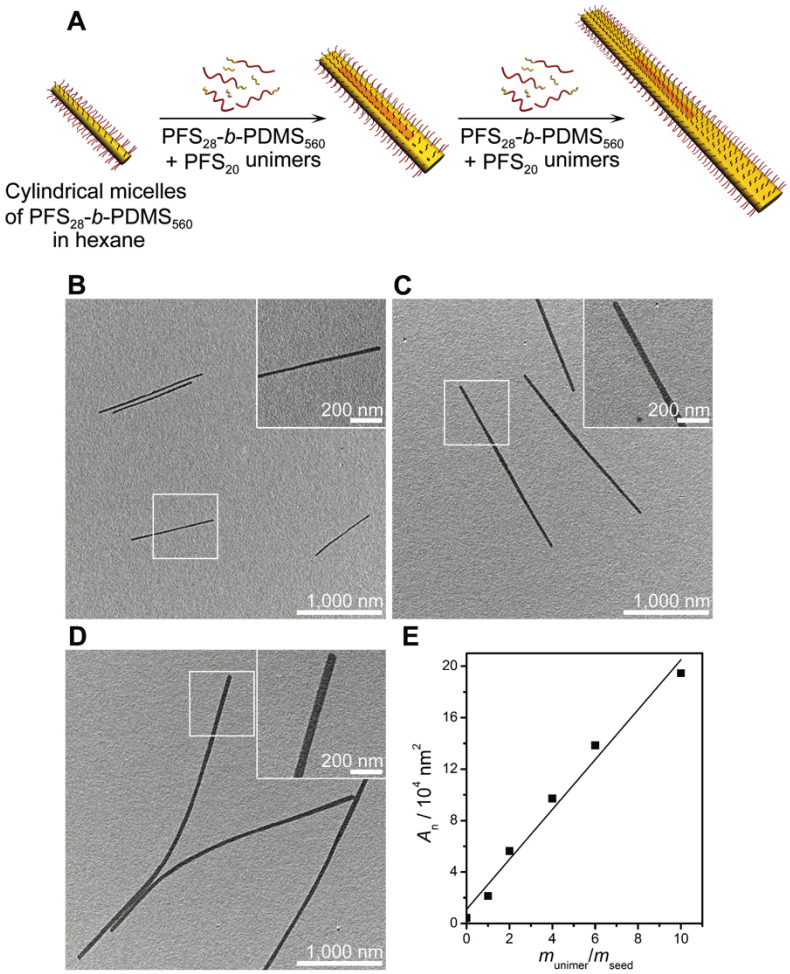

Fig. S3. Ribbon-like platelet micelles by seeded growth / living CDSA of PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} blends in hexane. Living CDSA of the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} blends can be initiated simultaneously from the ends and sides of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds. (**A**) Schematic diagram illustrating this process. (**B**–**D**) TEM images of ribbon-like micelles formed by the addition of the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} (1:1 mass ratio) blend unimers in a small amount of THF to a solution of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 340 nm) in hexane with unimer (total) to seed mass ratios of 1:1 (B), 4:1 (C) and 10:1 (D) at room temperature. (**E**) Linear dependence of micelle area on the unimer to seed mass ratio.

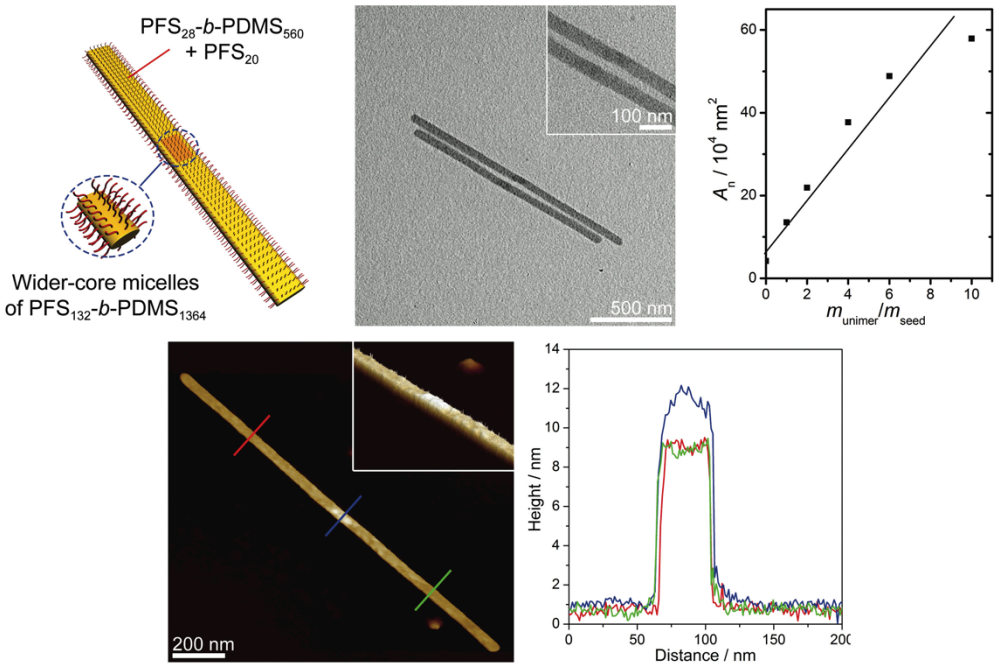

Fig. S4. Ribbon-like platelet micelles by seeded growth / living CDSA of PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} blends seeded by wider-core micelles. Schematic representation, TEM image, dependence of micelle area on the unimer to seed mass ratio, AFM height and 3D images (inset), and height profiles of ribbon-like micelles formed by a similar process in hexane at room temperature that was seeded by PFS_{132}-*b*-$PDMS_{1364}$ micelles (L_n = 120 nm) with a wider core (ca. 35 nm).

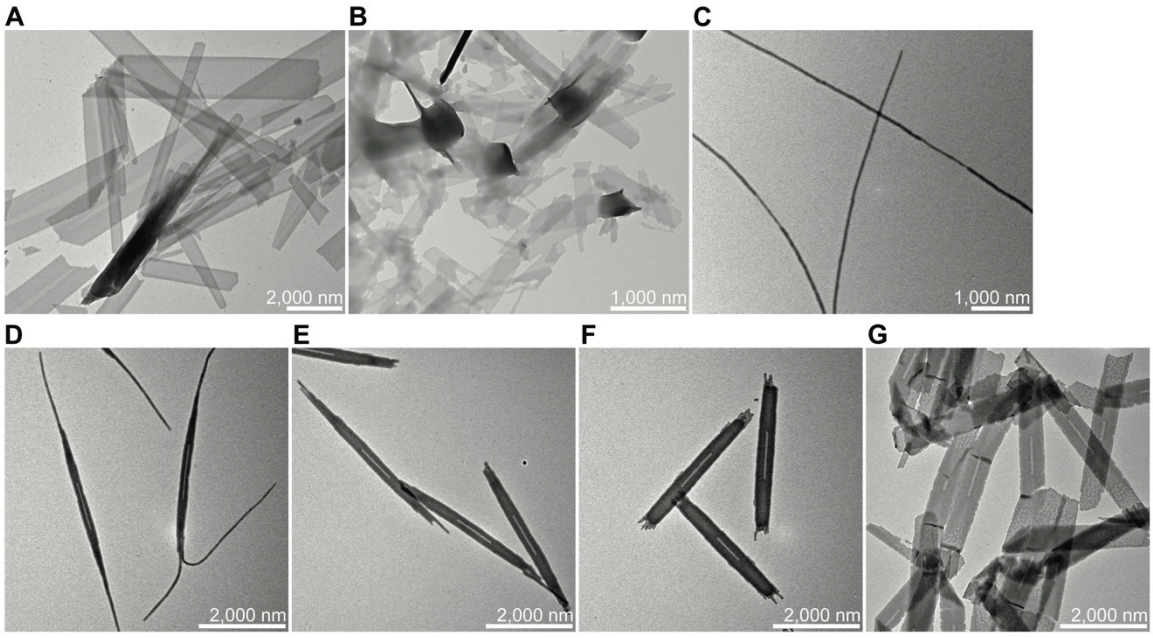

Fig. S5. Influence of seed and unimer composition on the formation of rectangular platelet micelles. (**A**) Irregular platelet micelles formed by homogeneous nucleation of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blends in a mixture of hexane and iPrOH (1:3, v/v) at 45 ºC in the absence of the cylindrical micelle seeds (see also ref. 37). (**B**) Irregular platelet aggregates formed by the addition of PFS_{20} unimers only to a solution of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 810 nm) in a mixture of hexane and iPrOH (1:3, v/v) at 45 ºC. (**C**) Cylindrical triblock comicelles formed by the addition of PFS_{36}-*b*-$P2VP_{502}$ unimers only to a solution of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 810 nm) in a mixture of hexane and iPrOH (1:3, v/v) at 45 ºC. (**D**-**G**) Micellar structures formed by the addition of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blend unimers to a solution of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 810 nm) in a mixture of hexane and iPrOH (1:3, v/v) at 45 ºC with PFS_{36}-*b*-$P2VP_{502}$: PFS_{20} mass ratios of 8:1 (**D**), 4:1 (**E**), 2:1 (**F**) and 2:3 (**G**), respectively.

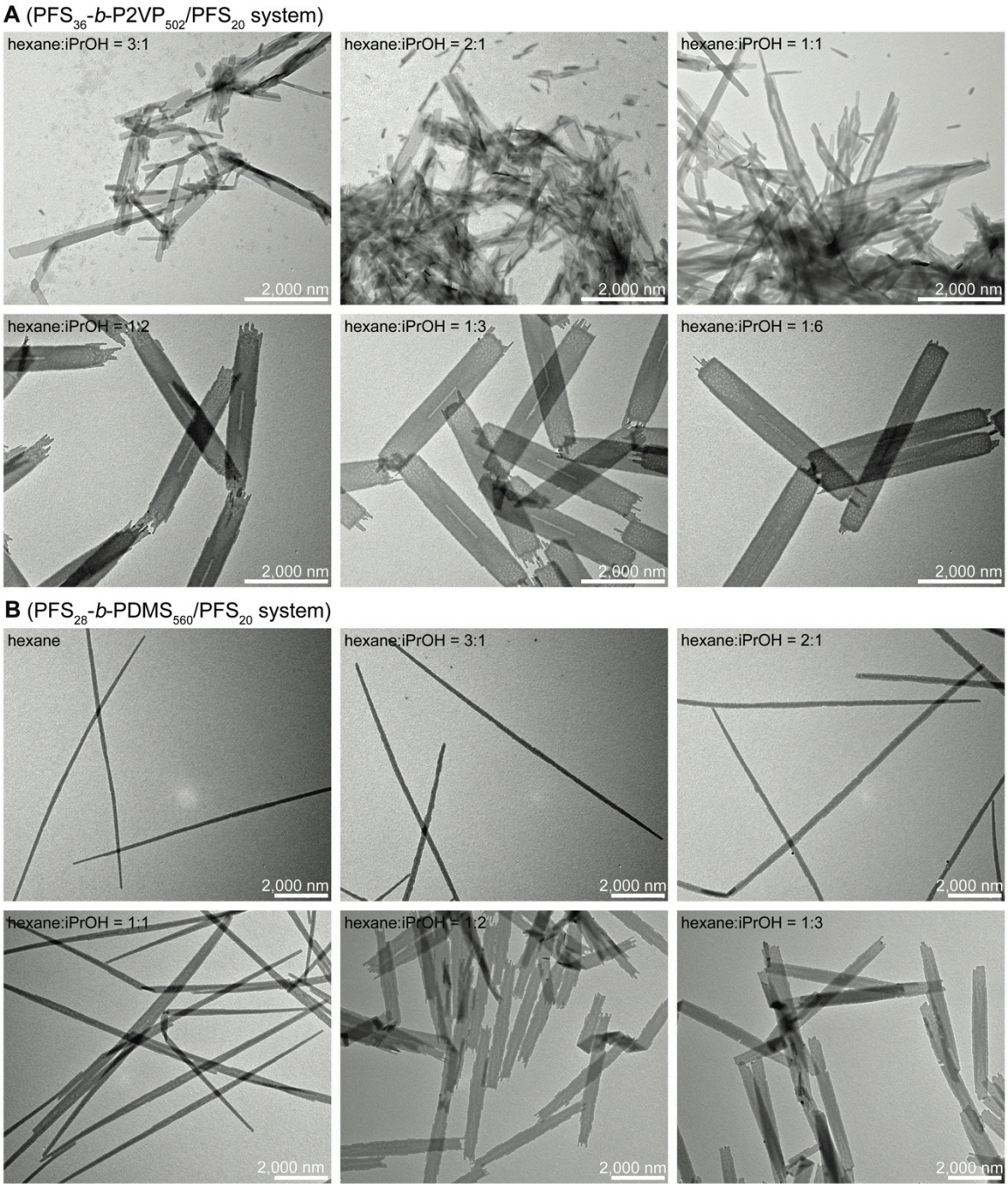

Fig. S6. Influence of solvent composition on seeded growth / living CDSA of PFS BCP/PFS homopolymer blends. The formation of rectangular platelet micelles can be facilitated in iPrOH-dominated hexane/iPrOH mixtures. (**A**) Micellar structures formed by living CDSA of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blends initiated by the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 810 nm) in hexane and various hexane/iPrOH mixtures (ratios in v/v) at 45 ºC. (**B**) Micellar structures from the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} blends using similar experimental procedures.

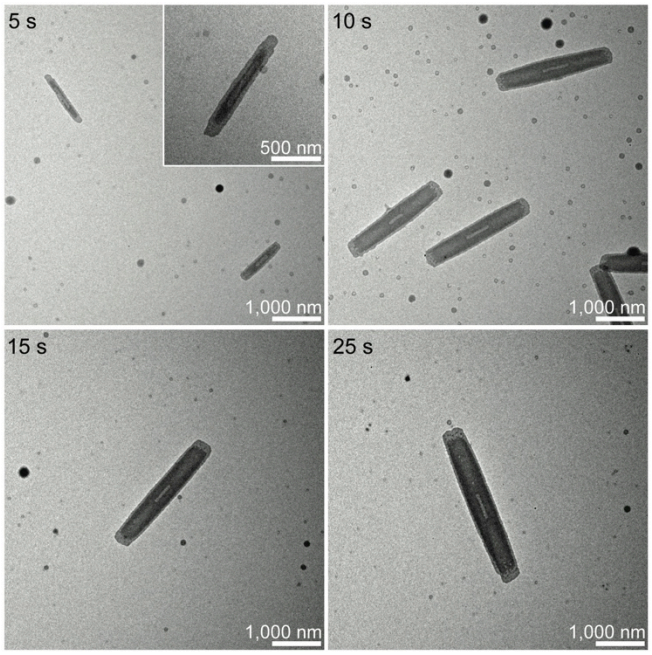

Fig. S7. Formation of rectangular platelet micelles by seeded growth / living CDSA monitored by TEM. TEM images (after solvent evaporation) showing the early stage growth process for the rectangular platelet micelles formed from PFS_{36}-*b*-$P2VP_{502}$: PFS_{20} = 1:1 blends initiated by the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 590 nm) in hexane/iPrOH 1:3 (v/v) at 45 ºC after 5 s, 10 s, 15 s, and 25 s. The growth completes within ca. 5 min and occurs by simultaneous lateral and terminal growth relative to the seed. The spherical structures of different size in the background are derived from unimers of the blend which have not yet grown from the platelet. These were no longer detected after 5 min. This study indicates that the rectangular platelet formation mechanism differs from that for lenticular micelle formation in which only BCP is added to a cylindrical seed where initial growth occurs from the micelle ends followed by a slow enveloping of the cylindrical seed (see the Figure 3 and associated discussion contained in ref. 19).

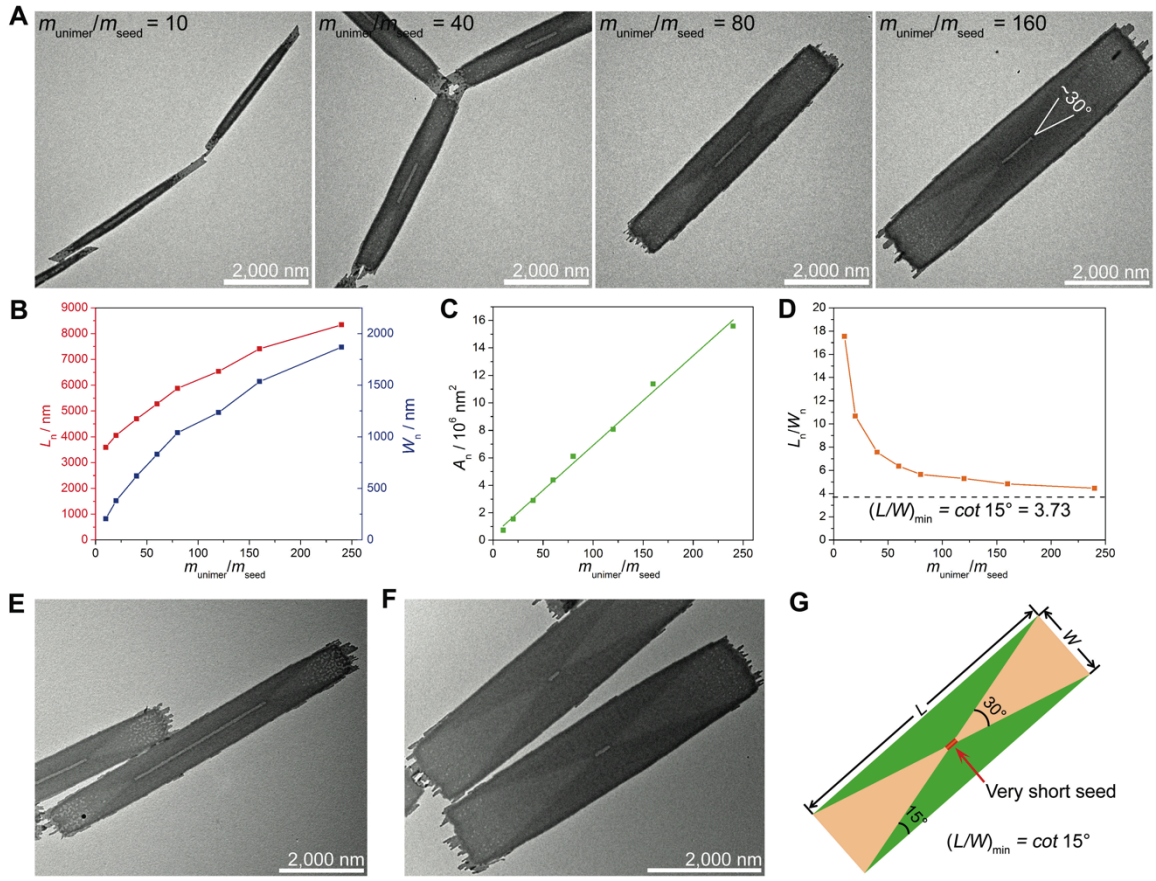

Fig. S8. Dimensional control of rectangular platelet micelles. The size and aspect ratio of the rectangular platelet micelles can be readily tailored. (**A**) TEM images of rectangular platelet micelles formed by living CDSA of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blends initiated by the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 810 nm) with various unimer to seed mass ratios at 45 ºC. (**B**) Dependence of L_n and W_n on the unimer to seed mass ratio. (**C**) Linear dependence of micelle area (A_n) on the unimer to seed mass ratio. **e**, Dependence of micelle aspect ratio (L_n/W_n) on the unimer to seed mass ratio. (**E** and **F**) TEM images of rectangular platelet micelles grown from relatively longer (E) and shorter (F) PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 2850 nm and 220 nm, respectively). (**G**) Schematic representation showing the dual-trapezoid texture and a minimum value of 3.73 (cot 15º) for the aspect ratio that could be expected when the dual-trapezoid texture spans the whole platelet and very short seeds are used. The dual-trapezoid structure appears to arise from the growth process and the resulting distribution of the crystallized blend components. Based on the AFM height analysis in Figure 1B the regions at the end of the seed are richer in PFS homopolymer.

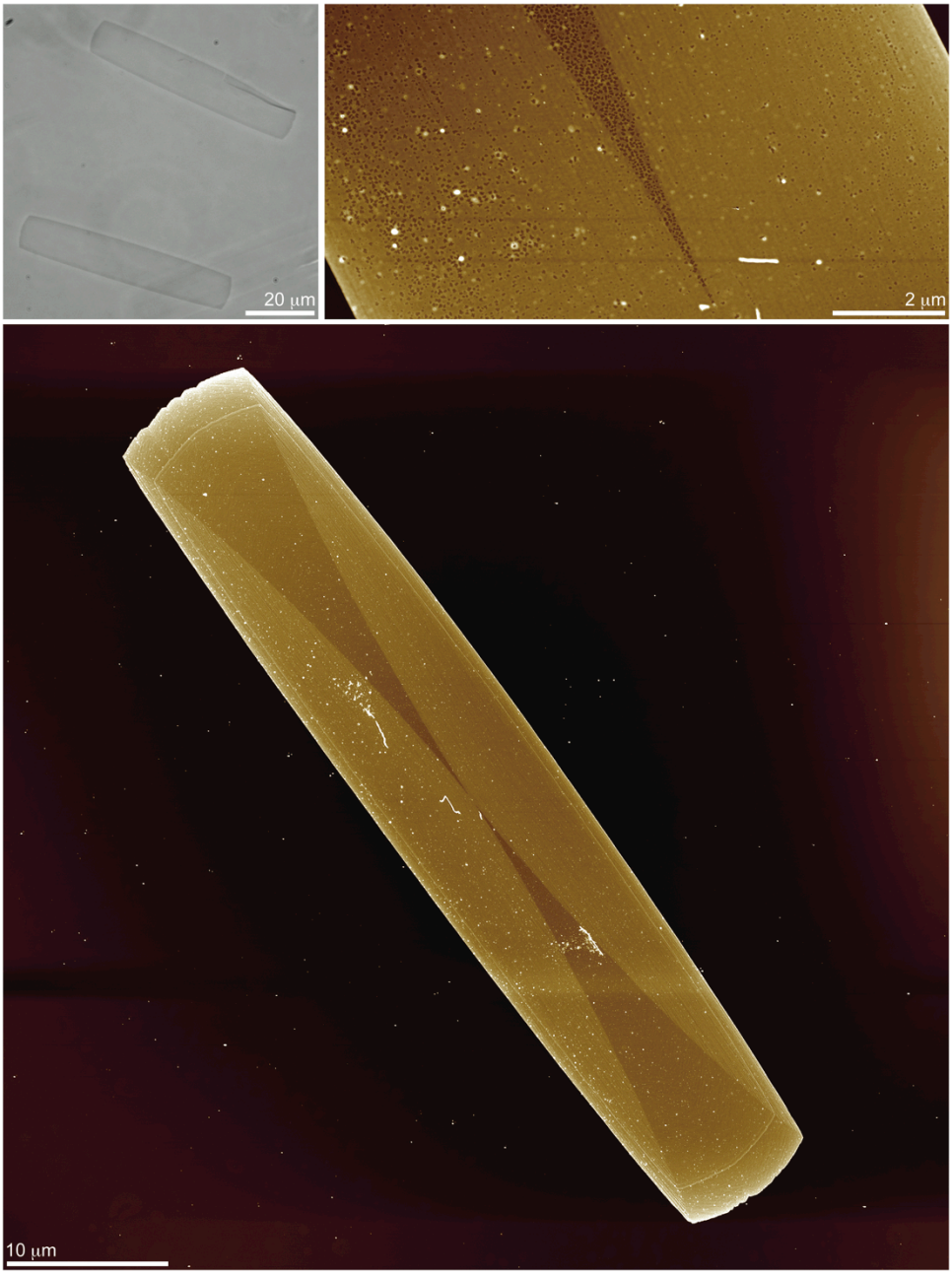

Fig. S9. Giant rectangular platelet micelles by seeded growth / living CDSA of PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blends. Taking the advantage of a slower living CDSA process in a mixture of hexane and methanol, the rectangular platelet micelles can grow up to more than 60 μm × 10 μm without any significant defects. Optical microscopy, TEM and AFM height images of rectangular platelet micelles formed by the addition of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} (1:1 mass ratio) blend unimers in a small amount of THF to a solution of the cylindrical micelle seeds of PFS_{20}-*b*-$P2VP_{444}$ (L_n = 970 nm, unimer to seed mass ratio = 5,000:1) in a mixture of hexane and methanol (1:3, v/v) at 45 ºC. The growth process took ca. 2 days. The lower solubility of PFS in methanol than in isopropanol is believed to render a slower growth rate.

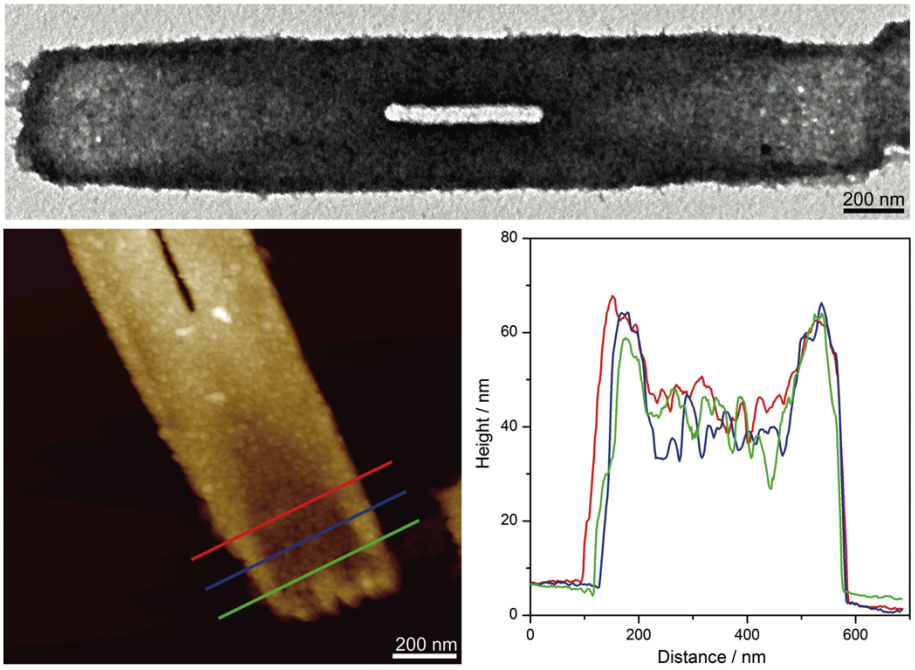

Fig. S10. Morphology of corona-crosslinked rectangular platelet micelles. High resolution TEM and AFM height images and height profiles of perforated rectangular platelets formed after crosslinking of the P2VP coronas via coordination of the pyridyl groups on P2VP with small Pt nanoparticles and subsequent redispersal in THF to remove the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelles seeds (L_n = 590 nm). The TEM images were obtained after 24 h and the AFM image after 1 year in THF.

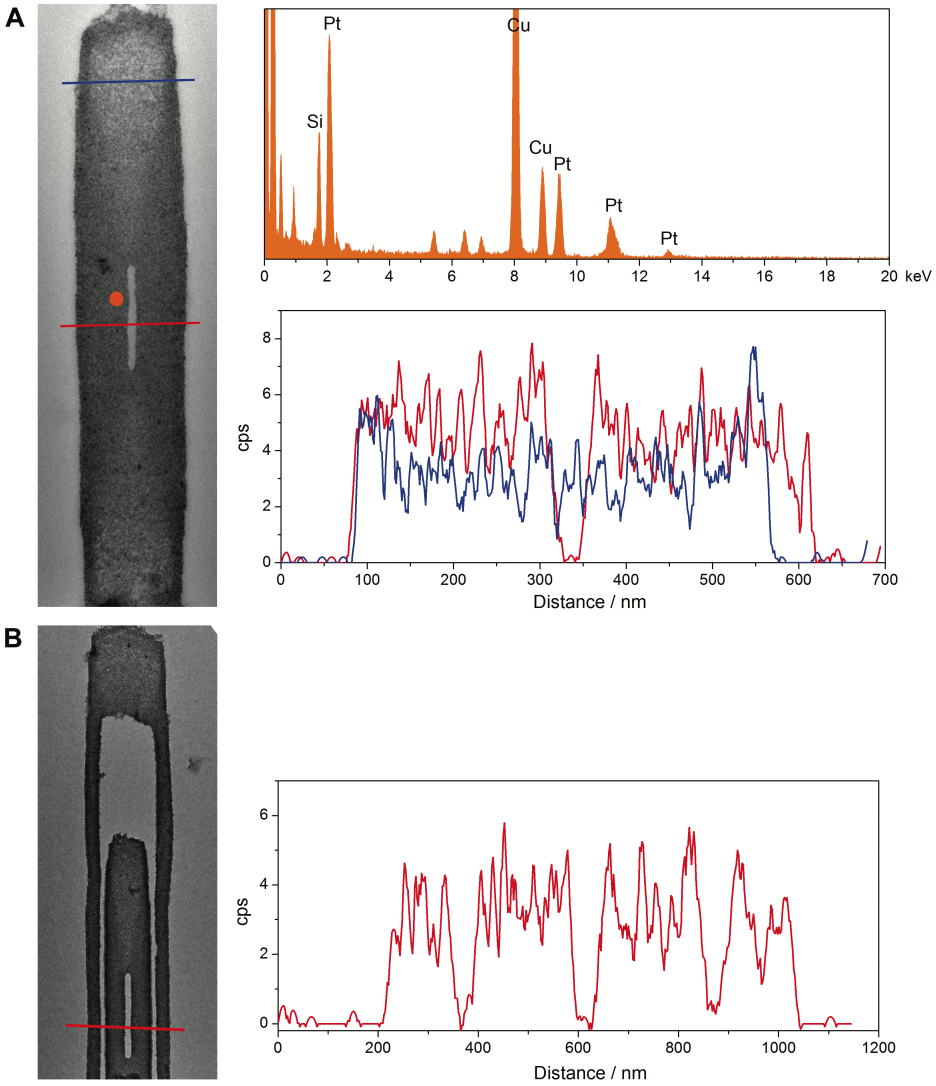

Fig. S11. Elemental composition of corona-crosslinked rectangular platelet micelles. (**A**) Spot and line-scan EDX analyses of the perforated rectangular platelets shown in the above figure to reveal the presence of Pt derived from the crosslinking Pt nanoparticles. The concentration of Pt appears higher in the regions lateral to the seed. In the EDX scans the Cu arises from the TEM grid. (**B**) Line-scan EDX analysis of a pair of perforated rectangular platelet and hollow rectangular ring form after redispersal of the crosslinked platelet block comicelles shown in Fig. 2C in THF.

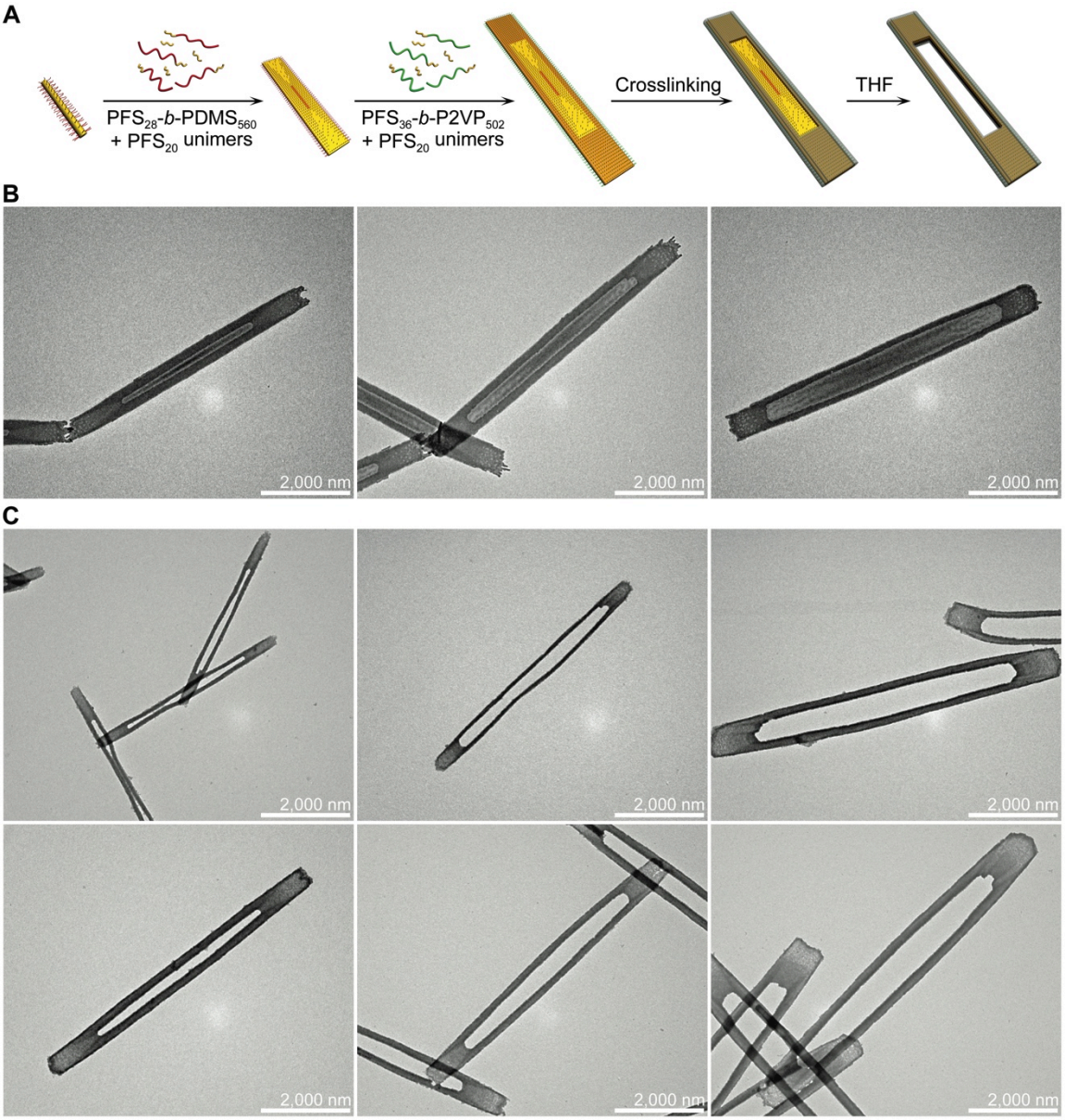

Fig. S12. Concentric rectangular platelet diblock comicelles and rectangular rings. Concentric rectangular platelet diblock comicelles can be formed through the sequential addition of the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} and PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blends. (**A**) Schematic diagram illustrating this process. (**B**) Representative TEM images of concentric rectangular platelet diblock comicelles formed by the sequential addition of the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} and PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} blend unimers (PFS BCP : PFS_{20} = 1:1 ratio) to a solution of the PFS_{28}-*b*-$PDMS_{560}$ cylindrical micelle seeds (L_n = 810 nm) in a mixture of hexane and iPrOH (1:3, v/v) at 45 ºC. (**C**) Representative TEM images of rectangular rings obtained after crosslinking of the P2VP coronas and redispersal in THF.

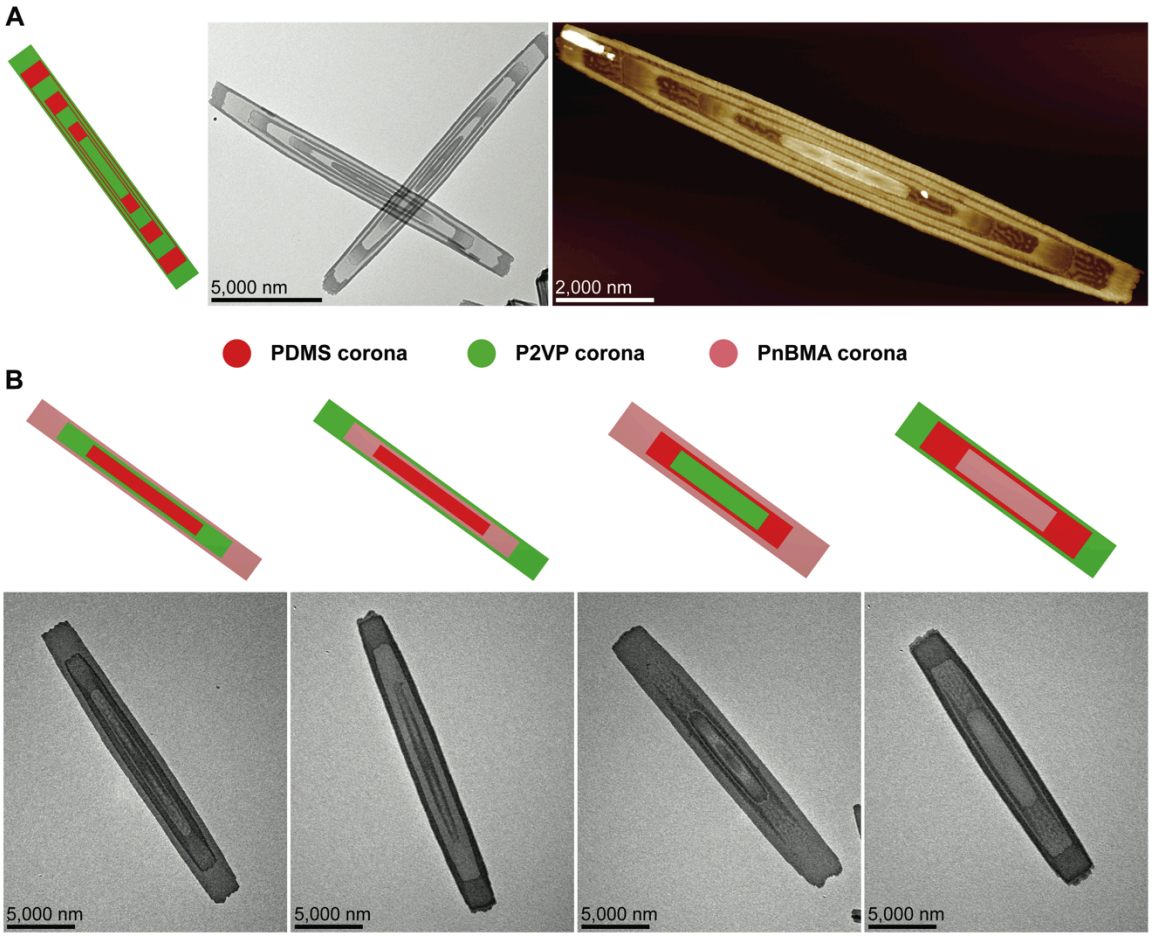

Fig. S13. Concentric rectangular platelet block comicelles with complex 2D constructions. Rectangular platelet multiblock comicelles can be prepared via the sequential construction of segmented regions with various corona chemistries. (**A**) Schematic representation, TEM image and AFM height image of concentric rectangular platelet heptablock comicelles formed by multiple, sequential alternate addition of the PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} and PFS_{28}-*b*-$PDMS_{560}$/PFS_{20} blend unimers (initial cylindrical seeds: PFS_{28}-*b*-$PDMS_{560}$ L_n = 810 nm). (**B**) Schematic representations and TEM images concentric rectangular platelet triblock comicelles formed by sequential alternating addition of the PFS_{28}-*b*-$PDMS_{560}$/PFS_{20}, PFS_{36}-*b*-$P2VP_{502}$/PFS_{20} and PFS_{36}-*b*-$PnBMA_{756}$/PFS_{20} blend unimers (initial cylindrical seeds: PFS_{34}-*b*-$P2VP_{272}$ L_n = 240 nm).

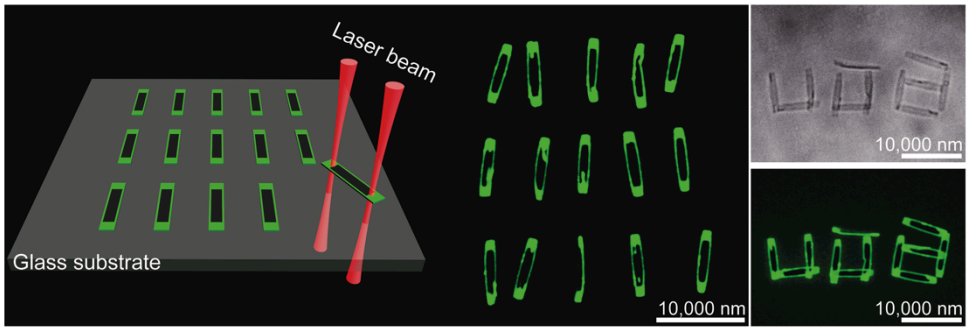

Fig. S14. Manipulation of rectangular platelets in solution. The rectangular platelet micelles and block comicelles possess excellent colloidal stability and are sufficiently robust to be manipulated. **a**, A 5 × 3 array and a customized pattern "UOB" (University of Bristol) of the fluorescent rectangular platelets fabricated by manipulation with optical tweezers in 1:3 (v/v) hexane/iPrOH and subsequent deposition using the hydrogen bonding interactions between the central P2VP coronas and the borosilicate substrate (*39*). The optical microscopy image was obtained on the optical tweezer system immediately after the deposition and the CLSM image was acquired using a confocal microscope after about 2 h.